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Atomic force microscopy and structural studies of MBE-grown CdF_2 layers on $CaF_2(111)$

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The wide bandgap (E_g = 8 eV) material CdF_2, doped with trivalent impurities, has well pronounced semiconducting properties. Bright electroluminescence (EL) has been observed in such crystals, with wavelength ranging from the IR to UV regions, depending on the dopant [1]. Recently, the feasibility of heteroepitaxial CdF_2 growth from a molecular beam on Si and CaF_2 surfaces has been demonstrated [2]. Therefore, fabrication of EL devices integrated with Si substrates would be very attractive. In our earlier studies [3], it was shown that, because of chemical interaction of CdF_2 molecules with Si surface at temperatures above 80–100°C, the crystalline quality of the layer quickly deteriorates with increase of the growth temperature. The post-growth annealing, usually employed to activate impurities in bulk CdF_2 [4], also presented problems for thin films on Si. There is , however, no the chemical interaction on CaF_2, so one can expect high quality growth at temperatures up to 600–700°C, when CdF_2 starts to sublime. Studies of doped CdF_2 growth at high temperatures are of interest for CdF_2 conversion in the semiconducting state without a postgrowth treatment.

In the present work, we apply Atomic Force Microscopy (AFM), Rutherford Backscattering Spectrometry/Channeling (RBS) and X-Ray Diffraction (XRD) to study the growth and structural perfection of Er-doped cadmium fluoride layers grown by Molecular Beam Epitaxy (MBE) on $CaF_2(111)$ substrates in a wide range growth temperatures range of 100–500°C.

Epitaxial growth and surface morphology of CdF_2 layers

$CdF_2/CaF_2(111)$ heterostructures were grown at the Ioffe Institute in a small research MBE system equipped with RHEED apparatus. Two effusion cells were loaded with small pieces of CaF_2 and CdF_2 crystals sublimated at 1300°C and 850°C respectively to obtain fluoride molecular beams. Before CdF_2 growth, a 200–300 nm thick CaF_2 buffer layer was grown at 770°C on carefully polished $CaF_2(111)$ substrates. The growth rate of CdF_2 layers was about 2–3 nm/min and the growth temperature was maintained within the 100–500°C range. Er doping was performed by exposing the growing CdF_2 surface to Er or ErF_3 beams from two other effusion cells. Table 1 presents the list of studied structures, together with their parameters obtained from AFM, RBS and XRD studies.

The surface morphology measurements have been carried out in the contact mode using an P4-SPM-MDT atomic force microscope produced by NT-MDT (Zelenograd, Russia). We found in AFM images that the surface morphology of CdF_2 layers strongly depends on the growth temperature. On the surface of layers grown at 100°C (Fig. 1a), one can see relatively small mounds with a lateral size of 30–60 nm and 2–4 nm in

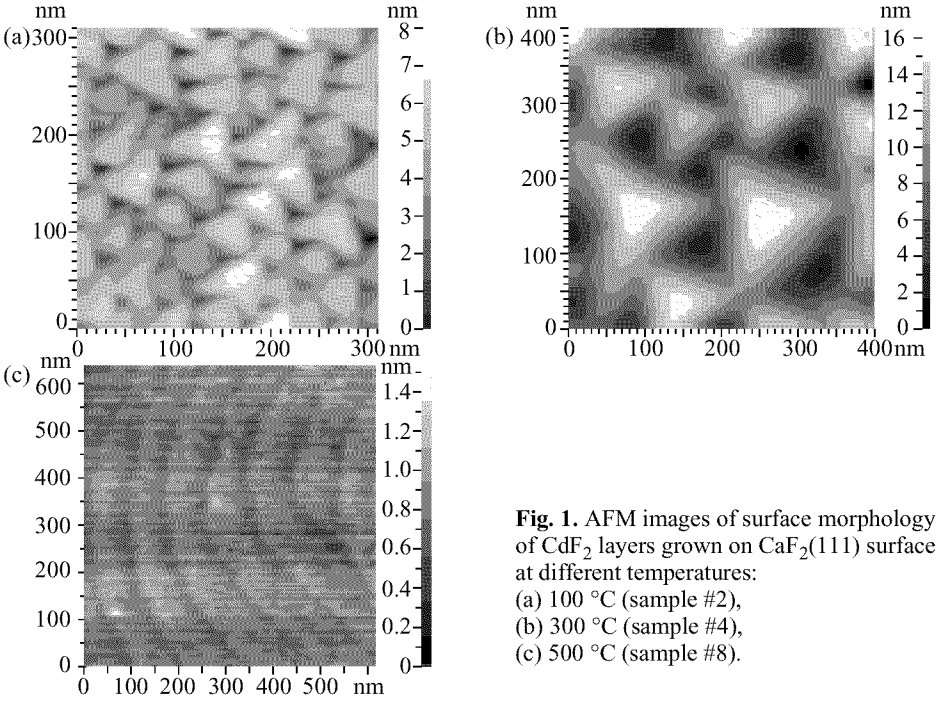

Fig. 1. AFM images of surface morphology of CdF_2 layers grown on CaF_2(111) surface at different temperatures:
(a) 100 °C (sample #2),
(b) 300 °C (sample #4),
(c) 500 °C (sample #8).

height. Some of them resemble triangular pyramids, others have no well-defined shape but still consist of the same type of facets. The surface of layers grown at 300°C has a similar but much more distinct morphology with noticeably larger facets (Fig. 1b). The average size of the pyramids increased to 150 nm and their height was about 10 nm. The angle between the facets and the (111) plane of the substrate was found to be about 10°, which corresponds to crystallographic planes (332) or is close to them. Similar low-angle mounds were observed during the epitaxial growth of Fe on Fe(100) [5] and numerous other studies. They are due to so-called Ehrlich-Schwoebel step barrier in interlayer diffusion [6, 7].

The surface morphology of CdF_2 layers grown at 400 and 500°C drastically changed. There were large round islands with lateral size of 1000–1500 nm and 4–12 nm in height. In general, the surface became much flatter and broad terraces (about 100 nm in width) between the monolayer (0.3 nm) steps were easily identifiable (Fig. 1c). Such 2D growth mode of fluorides on the (111) surface is expected at high temperatures because this surface has a minimum surface free energy in the fluorite-type structure [8].

RBS/channeling measurements

The RBS backscattering/channeling measurements were carried out on the Dynamitron accelerator at SUNY, Albany (USA). The 2 MeV $^4He^+$ ions and backscattering angle of 164 degrees were used. After a random spectrum was taken and all angles were set up for channeling measurement, the sample was shifted to a new spot to avoid the beam damage, which proved to be significant for CdF_2. The energy resolution of the system was estimated to be about 20 keV.

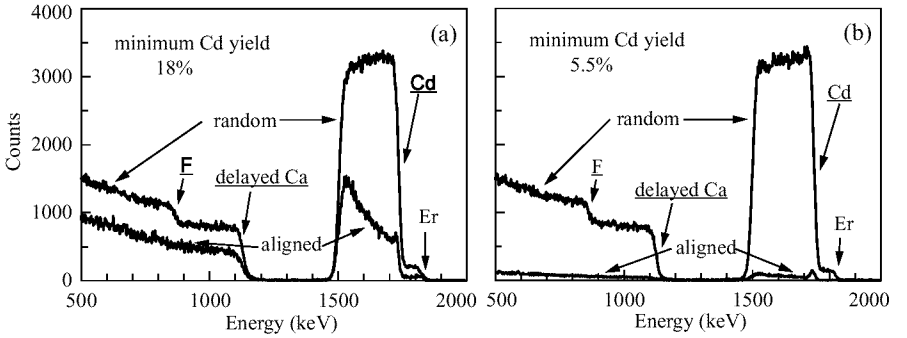

Fig 2. RBS random and aligned spectra for $CdF_2/CaF_2(111)$ heterostructures grown at different temperatures: (a) 100°C (sample #1), (b) 300°C (sample #5).

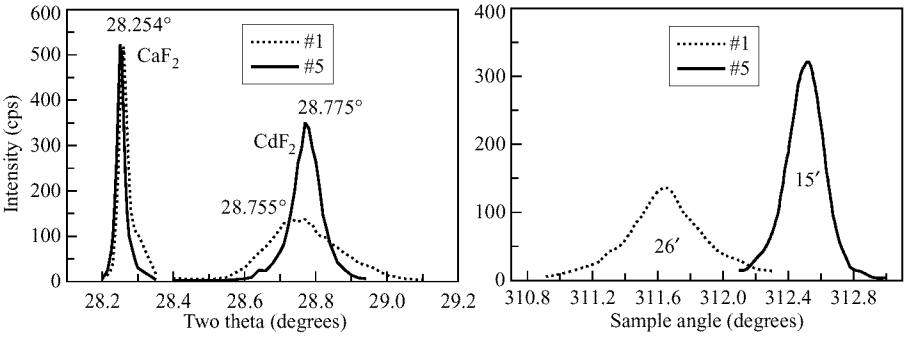

Fig 3. X-ray $\vartheta - 2\vartheta$ (a) and ω (b) diffraction curves from $CdF_2/CaF_2(111)$ heterostructures grown at 100°C (sample #1) and 300°C (sample #5).

Figure 2(a,b) presents the RBS/channeling data obtained for the $CdF_2/CaF_2(111)$ heterostructures grown at 100 and 300°C. As may be readily seen from the aligned to random signal ratio one, the CdF_2 layer in sample #5 is of much better crystalline quality, with the minimum Cd yield of only 5.5%. Another noteworthy feature is that the Er signal also decreases in the channeling orientation. This suggests that Er may occupy the substitutional rather than an interstitial position in the lattice, though a strict verification of this statement requires a channeling experiment along one more crystallographic direction. We plan to present these results at the conference.

XRD studies

The structural perfection of CdF_2 layers was studied on a high resolution triplecrystal diffractometer with the use of CuKα radiation and 111 symmetrical Bragg's reflection. Figure 3 shows the diffraction curves measured for the samples grown at 100 and 300°C. One can find from the $\vartheta - 2\vartheta$ curves (see Fig. 3a) that the relative difference in the interplanar spacing of the CdF_2 layer and the CaF_2 substrate for these two structures is equal to -1.71×10^{-2} and -1.79×10^{-2}, respectively. It is larger than expected from lattice mismatch for the bulk crystals ($\Delta a/a = -1.38 \times 10^{-2}$). This indicates the presence of residual strain. Both $\vartheta - 2\vartheta$ and ω-curves are broadened, which is typical for most systems with large mismatch and film thickness about 1 μ. The broadening

Table 1. Parameters of the studied CdF_2 layers.

No.	growth T (°C)	thick-ness (nm)	AFM type	AFM lateral size (nm)	AFM height (nm)	RBS χ_{min} (%)	XRD $\vartheta - 2\vartheta$ FWHM (arc.sec)	XRD ω-scan FWHM (arc.sec)
1(512)	100	330	M†	30–60	2–4	18	430	1560
2(514)	100	330	M	30–60	2–4	–	–	–
3(518)	200	330	M	60–100	4–5	–	320	2170
4(510)	300	370	M	100–150	8–10	–	–	–
5(513)	300	300	M	100–170	8–10	5.5	150	900
6(515)	300	330	M	100–150	8–10	–	–	–
7(519)	400	330	S‡	1000–1500	4–8	5.5	140	800
8(521)	500	570	S	1000–1500	4–12	–	120	750

† pyramidal mounds; ‡ round shape islands with 1 ML steps

can be related to randomly distributed threading dislocations. Both curves show that the crystal quality of the structures grown at 300°C is considerably higher.

Conclusions

The possibility of epitaxial CdF_2 growth on $CaF_2(111)$ substrates in a wide growth temperature range of 100–500°C has been demonstrated. It is found that there are pyramidal mounds on CdF_2 with a typical lateral size 30–60 nm at 100°C and 100–150 nm at 300°C. The angle between its facets and the growth plane is about 10°. At higher growth temperatures, the surface morphology drastically changes to large (1000–1500 nm) round islands formed by one-monolayer steps and 100 nm terraces. This indicates layer-by-layer growth. The RBS and XRD measurements show that the crystalline quality of the structures rapidly improves with the growth temperature.

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